5 isomer, 58502-27-5; **19** 5 isomer K salt, 58502-28-6; **20**, 15285-16-2; **20** H_2SO_4, 58502-30-0; **21**, 4928-87-4; sodium C_7N_7, 58502-31-1; tetramethylammonium C_7N_7, 58502-33-3; zinc $(C_7N_7)_2$, 58502-34-4; lithium C_7N_7, 58502-35-5; manganous $(C_7N_7)_2$, 58502-36-6; cupric $(C_7N_7)_2$, 58502-37-7; silver C_7N_7, 58502-38-8; tetraethylammonium C_7N_7, 58502, 39-9; trimethylactadecylammonium C_7N_7, 58502-40-2; *N*-methylphenazinium C_7N_7, 58526-69-5; trimethylsulfonium C_7N_7, 58502-42-4; methyltriphenylphosphonium C_7N_7, 58502-43-5; HC_7N_7, 58502-44-6; potassium cyanide, 151-50-8; cyanogen, 2074-87-5; sodium cyanide, 143-33-9; tetramethylammonium chloride, 75-57-0; zinc carbonate, 3486-35-9; 1-chloro-1*H*-imidazo[1,5-*b*]-*s*-triazole-2,5,7-tricarbonitrile, 58502-45-7; 1-methyl-1*H*-imidazo[1,5-*b*]-*s*-triazole-2,5,7-tricarboxamide, 58502-46-8; dimethylformamide, 68-12-2; 1-benzyl-1*H*-imidazo[1,5-*b*]-*s*-triazole-2,5,7-tricarbonitrile, 58502-47-9; benzyl chloride, 98-88-4; diazomethane, 334-88-3; 7-carboxamido-1-methyl-1*H*-imidazo[1,5-*b*]-*s*-triazole-2-carboxylic acid, 58502-48-0; 7-carboxamido-1-methyl-1*H*-imidazo[1,5-*b*]-*s*-triazole-5-carboxylic acid, 58502-49-1; sodium 7-carboxamido-1-methyl-1*H*-imidazo[1,5-*b*]-*s*-triazole-2-carboxylate, 58502-50-4; sodium 7-carboxamido-1-methyl-1*H*-imidazo[1,5-*b*]-*s*-triazole-5-carboxylate, 58502-51-5.

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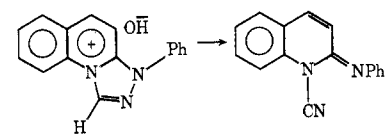

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Rearrangement of *N*-Acylaziridines in Strong Acid Media[1]

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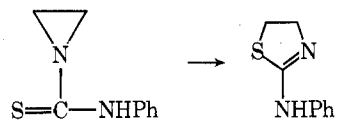
The rearrangement of *trans*-1-*p*-nitrobenzoyl-2,3-dimethylaziridine (**8**) in either sulfuric or fluorosulfuric acid occurs stereoselectively to give the *trans*-2-phenyl-4,5-dimethyloxazolinium cation and after neutralization the trans oxazoline **10**. In contrast, the isomeric cis aziridine derivative **7** gives a mixture of the cis and trans oxazolines, **9** and **10**, respectively, in a 28:72 ratio. These results implicate acyclic carbocationic intermediates in the rearrangement. The mechanism of the acid-catalyzed isomerization of acylaziridines is discussed in light of these results and other available data.

Gabriel and Stelzer[2] reported the acid-catalyzed isomerization of thioacylaziridines in 1895. Their report described the conversion of the thiourea derivative **1** to the thiazoline **2** upon heating the former in concentrated hydrochloric acid.

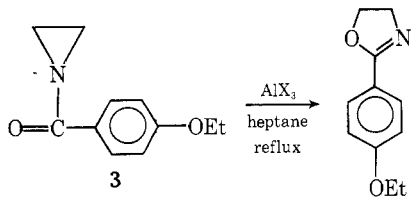


(1)

1 **2**

The reaction lay dormant until the late 1950s when a number of workers confirmed[3] and extended[4,5] the reaction.[6] One of these reports included isomerizations of several aziridines utilizing other aqueous mineral acid catalysts.[5]

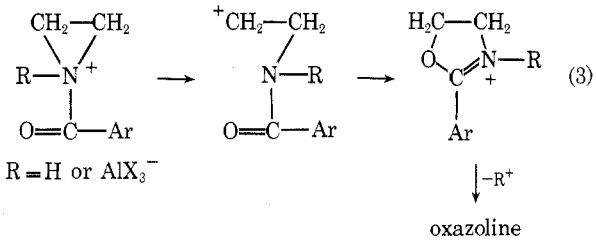
Heine and Proctor[7] carried out a similar isomerization on acylaziridines using aluminum halides in refluxing heptane, eq 2. Two mechanisms for the isomerization were considered;



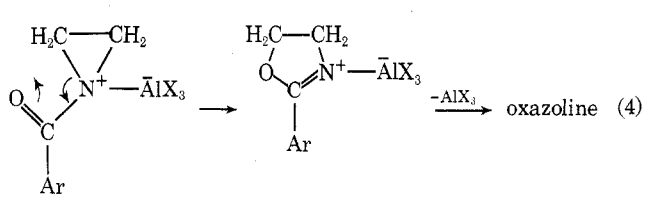
(2)

3

one involved sequentially acid attack at nitrogen, ring opening, and cyclization, eq 3; the second involved a four-centered transition state, eq 4. Owing to the low dielectric constant of



(3)



(4)

the solvent (heptane) and the high energy of the primary carbocationic intermediate formed from *N*-(*p*-ethoxybenzyl)aziridine (**3**), Heine and Proctor[7] preferred the mechanism shown in eq 4 for the isomerization of **3**.

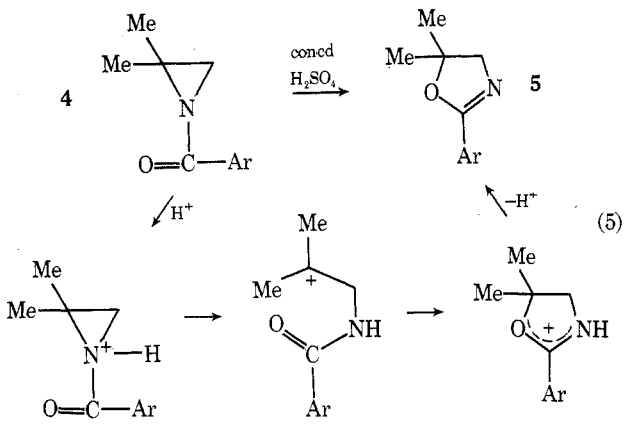
In subsequent work, Heine et al.[8] used concentrated sulfuric

Table I. NMR Data for 7, 8, 9, and 10[a,b]

Compd	Aryl protons	Methyl protons	Ring protons
7	8.16 (d), J = 9.1 8.23 (d), J = 9.1	1.35 (d), J = 5.5	2.66 (m)
8	8.10 (d), J = 9.0 8.24 (d), J = 9.0	1.23 (d), J = 5.2	2.56 (m)
9	8.09 (d), J = 9.0 8.25 (d), J = 9.0	1.25 (d), J = 6.4 1.38 (d), J = 6.0	4.52 (m, NCH) 4.89 (m, OCH)
10	8.04 (d), J = 8.7 8.14 (d), J = 8.7	1.31 (d), J = 6.7 1.42 (d), J = 6.0	3.86 (m, NCH) 4.33 (m, OCH)

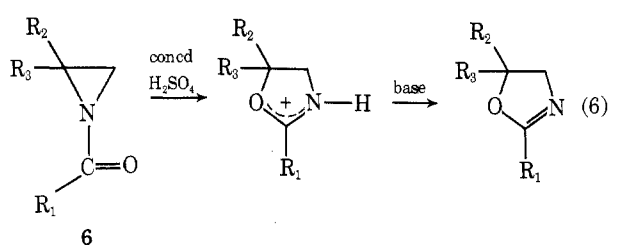
[a] Values are in parts per million from internal Me_4Si. Spectra were taken on Varian EM-360 and HA-100 spectrometers in $CDCl_3$. [b] d = doublet; m = multiplet.

acid as the medium for isomerizing 1-*p*-nitrobenzoyl-2,2-dimethylaziridine (**4**) to 2-*p*-nitrophenyl-5,5-dimethyl-2-oxazoline (**5**) in 97% yield. The sole formation of **5** and not the 4,4-dimethyl isomer was taken as evidence for scission of a C–N bond in a protonated aziridine. The mechanism shown in eq 5 was suggested to account for the observed reaction.



(5)

We have shown in an earlier paper[9] that *N*-acylaziridines (**6a–f**) rearrange to oxazolinium cations upon their introduction into strong acid media,[9–11] eq 6, and these ions are

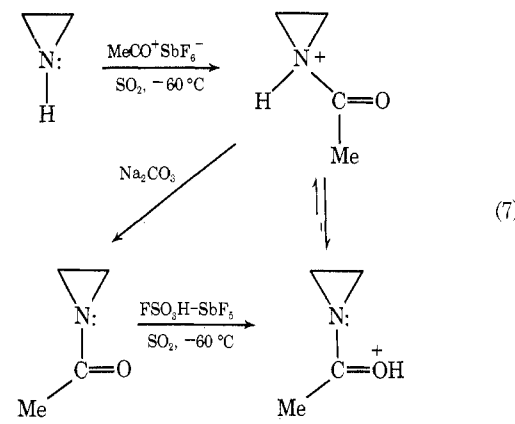


(6)

	R_1	R_2	R_3
a	CH_3	H	H
b	CH_3	CH_3	H
c	CH_3	CH_3	CH_3
d	C_6H_5	H	H
e	C_6H_5	CH_3	H
f	*p*-$NO_2C_6H_4$	CH_3	CH_3

stable[11,12] until neutralization by aqueous base. Demonstration of acyclic carbocationic intermediates or of N-protonated acylaziridines as precursors to oxazolinium ions in these isomerizations has not been achieved.

Olah and Szilagyi[13] have prepared N-protonated acylaziridines from the reaction of aziridine and acylium salts, eq 7. Conversely, direct protonation of acylaziridines at low temperature provides, as the only protonated species (by NMR analysis), the O-protonated acylaziridine.[9,13] Olah and Szilagyi[13] suggested that an equilibrium exists between the O-protonated and the N-protonated forms (see eq 7), but did not produce compelling evidence in favor of it.

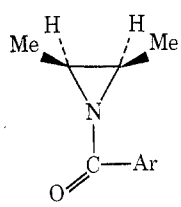


(7)

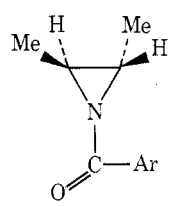
The present study of the acid-catalyzed rearrangement of *cis*-(**7**) and *trans*-(**8**) 1-*p*-nitrobenzoyl-2,3-dimethylaziridine provides the first published account on the stereochemistry of isomerization of acylaziridines in strong acid media.

Results and Discussion

The acylaziridines **7** and **8**, dissolved in carbon tetrachloride, were readily extracted into cold 90% sulfuric acid solution or into fluorosulfuric acid resulting in solutions which gave NMR spectra characteristic of oxazolinium cations. However, the spectra were complex, making an unequivocal stereochemical assignment of the structures difficult. Therefore, the fluorosulfuric acid solutions of **7** and of **8** were drowned into cooled and rapidly stirred aqueous potassium carbonate–ether solutions.[14] Upon drying of the ether layers and removal of the ether, the resulting oxazolines were obtained. Analysis of the NMR spectra of the products was performed. The NMR spectrum of the rearrangement products of the cis isomer **7** was complex; however, it was interpreted by assuming that a mixture of **9** and **10** was present. The isomerization product

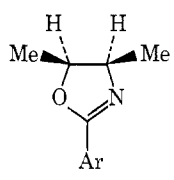


7

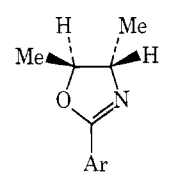


8

Ar = *p*-nitrophenyl

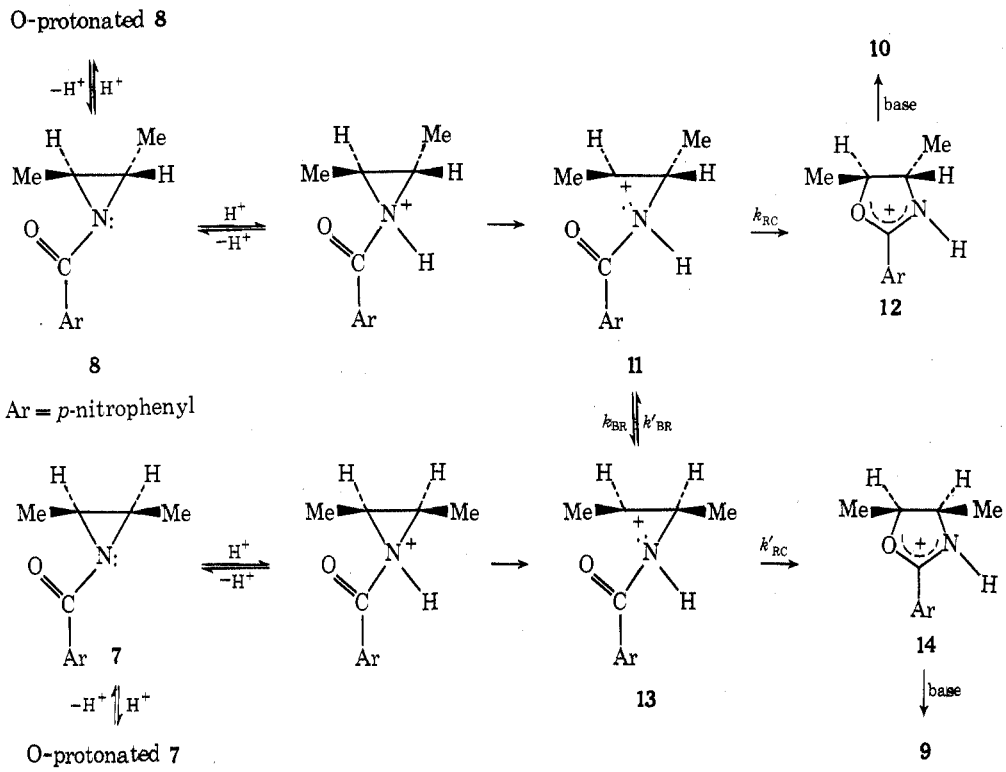


9



10

Scheme I



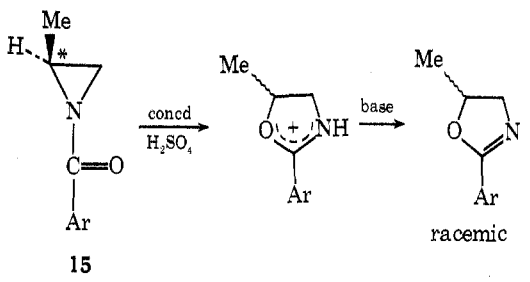
of the trans isomer 8 gave an NMR spectrum consistent with a single component which was shown to be the trans oxazoline 10 by comparison with an authentic sample.[15] The NMR data for the aziridines and oxazolines are shown in Table I.

Gas chromatographic (GC) analysis of the product of isomerization of 8 in fluorosulfuric acid revealed a single peak due to 10.[15] In agreement with the NMR analysis, GC analysis of the product of rearrangement of 7 revealed a 28:72 mixture of the cis (9) and trans (10) oxazolines, respectively.

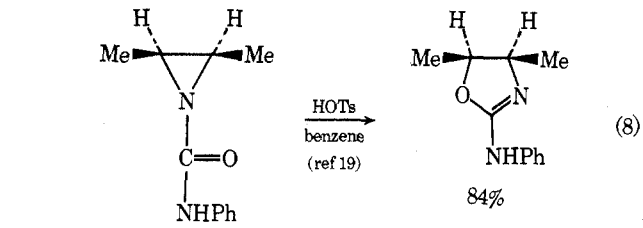
Our results show that 8 stereoselectively rearranges to 10 while 7 shows little selectivity. The finding of stereoselectivity in the rearrangement of the trans aziridine 8 and the lack of stereoselectivity in the rearrangement of the cis isomer 7 confirms Heine's suggestion of acyclic carbocation involvement as shown in eq 5. Our view of how these reactions occur is shown in Scheme I. It is reasonable to assume that these rearrangements occur via the N-protonated acylaziridines. The differences in the products can be accounted for by assessing the probable fates of the carbocations 11 and 13. Since the trans oxazolinium ion 12 does not suffer from nonbonding interactions of the severity of those in 14, the transition state leading to 12 should be preferred to that leading to 14. Thus upon opening of the N-protonated aziridine ring of 8, ring closure of the carbocation 11 to the oxazolinium ion 12 would be highly favored over bond rotation (i.e., $k_{RC} > k_{BR}$) to give carbocation 13 which subsequently could undergo ring closure to 14. The finding of a mixture of 9 and 10 from the rearrangement of 7 indicates that bond rotation in 13 (i.e., 13 → 11) competes with ring closure to 14 (i.e., $k'_{BR} \simeq k'_{RC}$). From these results it seems likely that if substituents substantially larger than methyl groups were present in a cis aziridine like 7, the product upon acid-catalyzed rearrangement may well be solely the trans oxazoline.

Hearn[17] has studied the isomerization of (*S*)-1-*p*-nitrobenzoyl-2-methylaziridine (15) in concentrated sulfuric acid and observed a significant amount of racemization.[18] His results tend to support the mechanism presented in Scheme I.

Nabeya and Iwakura and their co-workers[19,20] have investigated the stereochemistry of the acid-catalyzed isomerization of 1-carbamylaziridines to 2-amino-2-oxazoline derivatives and have obtained results which are remarkably different from ours. This is undoubtedly the result of their use of nonpolar solvents with low ionizing power whereas our solvents are highly polar and highly ionizing. Hence the SN1-like mechanism, which we propose for isomerization of acylaziridines in strong acids such as sulfuric and fluorosulfuric, is not favored in nonpolar solvents owing to the relative instability of carbocations in nonpolar media.[21] The results of isomerization with *p*-toluenesulfonic acid of some carbamylaziridines in refluxing benzene are shown in eq 8–10. Without additional evidence, one might suggest that the result shown in eq 8 is explicable by a carbocationic mechanism, that is, an intimate ion pair might result between the carbocation and the conjugate base of the acid (i.e., OTs^-). Collapse of such an ion pair in benzene would undoubtedly be rapid; hence stereochemistry might be retained. The results shown in eq 9, however, negate the above proposal as the sole mechanism. Since a portion of the product is obtained from aziridine ring opening at the less substituted carbon,[22] at least some of the product (and perhaps most of it) must arise by another mechanism. The most likely alternative mechanisms[19,20] are one similar to that shown in eq 4 and an SN2-like mechanism similar to that known for nucleophile-catalyzed isomerization of acylaziridines.[6,16] The results shown in eq 10 are best explained by the intimate ion pair mechanism.[20] Thus, when no unbound counterion is present (as in the boron trifluoride cat-



Ar = *p*-nitrophenyl



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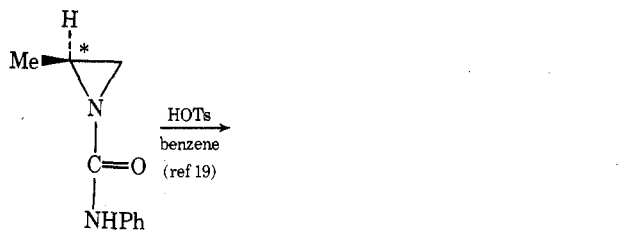

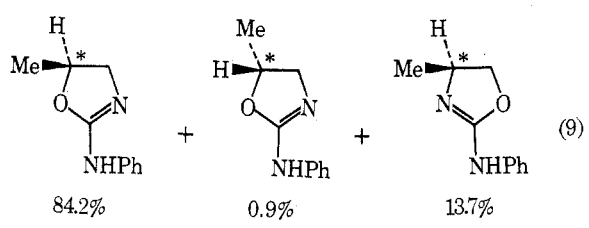

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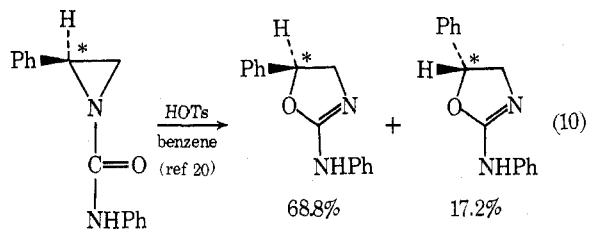

(10)

alyzed reaction), the product is nearly racemized,[20] indicating a mechanism change to one involving a free carbocation.

In summary, the acid-catalyzed isomerization of acylaziridines occurs via acyclic carbocation intermediates in strong acid media. The stereochemistry of the products appears to be determined by a competition between the rates of cyclization and of bond rotation, processes which are affected by nonbonded interactions. In nonpolar media, acyclic carbocations do not appear to be involved except where carbocation stabilizing groups, such as an aryl group, are present. In the latter cases, with protonic acids intimate ion pairs appear to be involved in determining product stereochemistry.

Experimental Section

***erythro-* and *threo*-3-Amino-2-butanol.** The isomeric 3-amino-2-butanols were prepared by the ammonolysis of the respective epoxides by the procedure previously reported.[23] A mixture of *cis*-2,3-epoxybutane and *trans*-2,3-epoxybutane (Research Organic/Inorganic Chemical Corp.) was separated by careful distillation with a Nester-Faust adiabatic annular Teflon spinning band assembly in a manner similar to that described by Dickey et al.[24] Refractionation of the purified fractions gave the trans epoxide, bp 55–56 °C (lit.[24] 54–55 °C), and the cis epoxide, bp 59–60 °C (lit.[24] bp 58–59 °C).

Reaction of the cis epoxide with excess liquid ammonia in the presence of 1 equiv of water, as described elsewhere,[23] gave a 90% distilled yield of *threo*-3-amino-2-butanol, bp 69–70 °C (20 mm). The erythro isomer was prepared in a similar fashion from the trans epoxide. The crude amino alcohol was used to prepare the trans aziridine as described below.

***cis*-1-*p*-Nitrobenzoyl-2,3-dimethylaziridine (7).** *cis*-2,3-Dimethylaziridine was prepared from *threo*-3-amino-2-butanol following the directions of Dickey et al.[24] The purified aziridine, bp 82–83 °C (lit.[24] bp 82.5–82.9 °C), was converted to the amide **7** by reaction with freshly recrystallized *p*-nitrobenzoyl chloride and triethylamine in dry benzene by the procedure of Heine et al.[16] Recrystallization from ethanol gave **7** melting at 142–143 °C (lit.[16] 143–145 °C). The NMR spectrum of **7** (see Table I) was consistent with the assigned structure.

Isomerization of 7 and 8 in 90% Sulfuric Acid. A carbon tetrachloride solution containing ca. 10% of **8** was added dropwise to an equal volume of a rapidly stirred 90% sulfuric acid solution at 10–15 °C. After about 10 min of rapid stirring below 15 °C, the sulfuric acid layer was transferred to an NMR tube and a capillary filled with tetramethylsilane was added. The NMR spectrum had peaks at δ 1.96–2.15 (6 protons, broad multiplet, CHC), 4.98–5.40 (1 proton, broad multiplet, CHN), 5.50–5.90 (1 proton, broad multiplet, CHO), 8.55 (2 protons, doublet, J = 8.5 Hz, aryl), 9.02 (2 protons, doublet, J = 8.5 Hz, aryl), and 9.76 ppm (1 proton, broad NH). This spectrum was consistent with that of oxazolinium ions **12** or **14** but was too poorly resolved to allow a definitive stereochemical assignment.

In the same manner, a small sample of **7** was dissolved in 90% H_2SO_4 and the NMR spectrum of the resulting solution was recorded. All of the peaks above plus additional peaks were present.

Isomerization of 7 and 8 in Fluorosulfuric Acid. The acylaziridines **7** and **8** each in ca. 10% carbon tetrachloride solutions were extracted into fluorosulfuric acid[9] at 0 °C using the technique described above. The acid solutions were allowed to warm to room temperature and their NMR spectra were recorded. The spectra of the protonated oxazolines in FSO_3H appeared to be very similar to the spectra of the ions in 90% H_2SO_4.

The FSO_3H solutions were neutralized by dropwise addition to rapidly stirred dispersions of aqueous potassium carbonate–ethyl ether.[14] The ether layers were dried (Na_2SO_4) and evaporated to give the crude isomerization products from **7** and from **8**.

The NMR spectrum of the dried product from the isomerization of **8** proved to be identical with that of an authentic sample[15] of **10** (see Table I). Gas chromatographic analysis on a 6 ft × 0.125 in. silicone gum W-98 column showed the isomerization product from **8** to be solely **10** (i.e., with less than 0.5% of **9**).

The dried product from the isomerization of **7** gave an NMR spectrum (in CCl_4) indicating a mixture. A comparison analysis of the spectrum of this sample with those of authentic samples of **9** and **10** (see Table I) proved the mixture to be composed of **9** and **10**. Gas chromatographic analysis under identical conditions with those above revealed the mixture to be **9** and **10** in a ratio of 28:72.

It was also shown that **9** and **10** do not equilibrate under workup or analytical conditions and that the cations in sulfuric or fluorosulfuric acid do not equilibrate.[12] It could not be unequivocally demonstrated that **7** does not partially isomerize to **8** prior to rearrangement; yet there is no evidence that this is occurring.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also kindly acknowledge a gift of authentic samples of **9** and **10** by Professor Harold W. Heine.

Registry No.—**7**, 7042-44-6; **8**, 7042-45-7; **9**, 7042-06-0; **10**, 7042-07-1; *cis*-2,3-dimethylaziridine, 930-19-8; *p*-nitrobenzoyl chloride, 122-04-3.

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Versatile Intermediates for Heteroatom-Substituted Adamantane Derivatives

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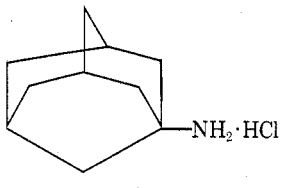
9-Acetoxybicyclo[3.3.1]nona-2,6(7)-diene (**18**), a versatile intermediate for the synthesis of heteroatom substituted adamantanes, was prepared in eight steps from the commercially available 1,4-cyclohexanediol. This intermediate may be used in the synthesis of substituted oxa-, aza-, and thiaadamantanes. Utility of this intermediate was shown by synthesis of 2-oxa-6-adamantanol (**19**), 2-oxa-6-adamantanone (**22**), 2-oxa-6-adamantanamine hydrochloride (**23**), and 2-oxa-6-adamantanecarboxylic acid (**26**).

There has been much interest in compounds containing the adamantane moiety since they exhibit many interesting medicinal properties. Adamantane derivatives have shown effectiveness against several types of viruses,[1-4] and in treatment of leukemia.[5] They were also found to be active in vitro against angeosarcoma, pancreatic sarcoma,[6] and antineoplastic activity.[7-9] Davies et al.[10] discovered the inhibitory effects of 1-adamantanamine hydrochloride (**1**) against in-



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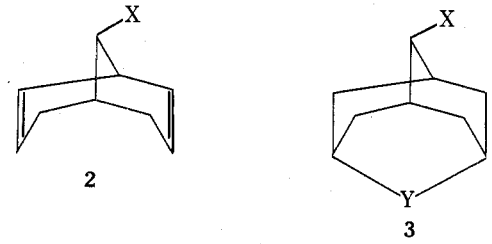
fluenza group A. 1-Adamantanamine was also found, quite by accident, to be active against Parkinson's disease.[11]

In view of the ability of adamantane to modify the biological activity of various compounds and the importance of heteroatoms in medicinal chemistry, we launched a program to synthesize adamantane derivatives with a heteroatom (oxygen, nitrogen, or sulfur) incorporated in the adamantane ring system.[12] We report here the synthesis of versatile intermediates for heteroatom-substituted adamantanes, and the synthesis of 2-oxaadamantan-6-amine and 2-oxaadamantane-6-carboxylic acid.

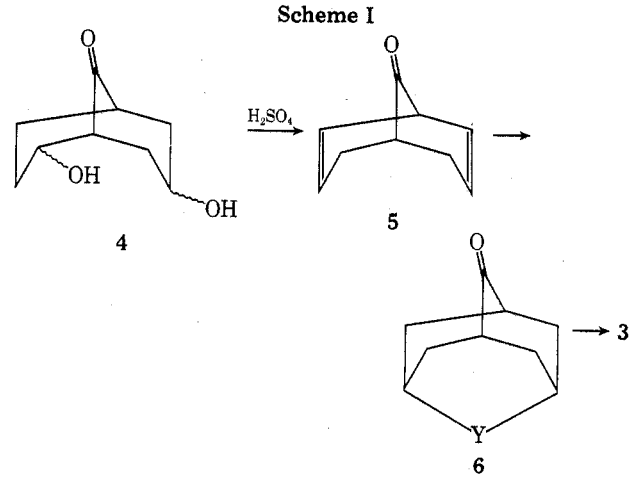
The immediate goal was to synthesize 9-substituted derivatives of bicyclo[3.3.1]nonadiene (**2**). Our long-range goal was to synthesize 2-substituted heterocyclic compounds **3** of the adamantane series through the intermediacy of compound **2**. The envisioned synthesis that was proposed for the aforementioned goals is depicted in Scheme I.



2 **3**

X = OH, OTs, NH_2, COOH
Y = O, N, S

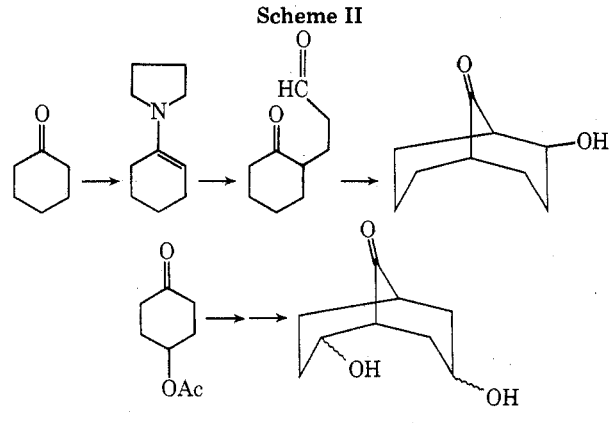
Scheme I



4 **5** **6**

Our plans for accomplishing the synthesis of the diol **4** involved modification of a procedure originally worked out by Cope[13] and Woodward.[14] If these procedures were now applied to 4-acetoxycyclohexanone, compound **4** should result (Scheme II).

Scheme II



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